

UNIT III: CHEMISTRY OF MATERIALS

Part- A: Nano materials:- Introduction-sol-gel method-characterization by BET, SEM and TEM methods applications of graphene-carbon nanotubes and fullerenes:Types, preparation and applications Thermal analysis techniques: Instrumentation and applications of thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC).

Part-B: Refractories: - Definition, classification, properties (refractoriness, refractoriness under load, porosity and thermal spalling), failure of refractories. Lubricants: - Definition, mechanism of lubricants and properties (definition and importance). Cement: - Constituents, manufacturing, parameters to characterize the clinker formation: lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR), chemistry of setting and hardening, deterioration of cement.

Part- A: Nano materials:

1) Explain top-down and bottom-up approach for nanomaterial preparation with examples.

The nanomaterials can be synthesized in two ways, namely Bottom-up approach and Top-down approach

Bottom-up approach:

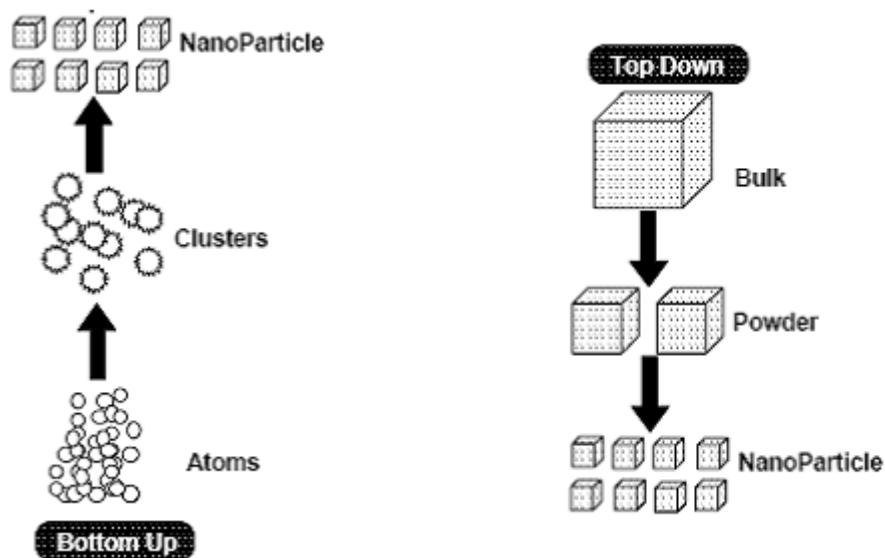
In this method, the nanomaterials are synthesized by assembling the atoms and molecules together.

Examples: Ball milling and Sol-gel method.

Top-down approach:

In this method, the nano materials are synthesized by dis-assembling the solids into finer pieces until the particles are in the order of nanometres.

Examples: plasma arching, chemical vapour deposition method.



2) Define nano materials? Describe sol-gel method of synthesis of nano materials?

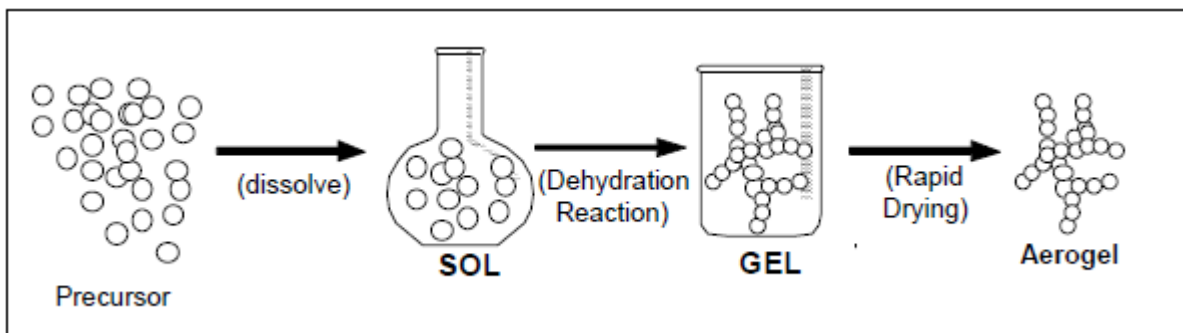
Nano materials: Nano materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.

Sol-Gel process:

This is an example for Bottom-Up approach comes under chemical method.

Examples: Zinc oxide nanoparticles, TiO_2 nanoparticles can be synthesized by this method.

The sol-gel process is a wet technique i.e., chemical solution deposition technique used for the production of high purity and homogeneous nanomaterials.



a) preparation of sol: In this method, metal alkoxide is used as a precursor to synthesize nanoparticles of a metal oxide. Metal alkoxide is dissolved in alcohol and then water is added under acidic, neutral or basic conditions. Addition of water leads to hydrolysis in which alkoxide ligand is replaced with a hydroxyl ligand.

b) Conversion of sol to gel: The polycondensation reaction between MOR and MOH results in the formation of an oxide - or alcohol- bridged networked gel.

c) Aging of the gel: The reaction mixture is allowed to continue polycondensation reactions until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.

d) Removal of a solvent: The water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting product is termed a xerogel. If the solvent is extracted under supercritical conditions, resulting product is termed an aerogel.

e) Heat treatment: The sample obtained is calcined at high temperature to obtain nanoparticles. Nanoparticles formed by sol-gel process commonly have a size ranging from 1 to 100 nm.

Advantages:

1. Nanomaterials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical characteristics resulting materials.
4. Simple and inexpensive equipment.

3) Explain BET technique for characterization of nano materials?

Brunauer–Emmett–Teller (BET) theory aims to explain the physical [adsorption](#) of [gas molecules](#) on a [solid surface](#) and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The BET theory refers to multi layer adsorption, and usually adopts non-corrosive gases (like nitrogen, argon, carbon dioxide, etc.) as adsorbates to determine the surface area data.

- ❖ Gas sorption (both adsorption and desorption) on the clean surface of dry solid powders is the most popular method for determining the surface area and pore size distribution of nanomaterials.
- ❖ In a gas sorption experiment, the material is heated and degassed by vacuum force or inert gas purging to remove adsorbed foreign molecules.
- ❖ Controlled doses of an inert gas, such as nitrogen, krypton, or argon, are introduced and the gas is adsorbed, and later, withdrawn and desorbed.
- ❖ This cycle of adsorption and desorption is carried out several times.

- ❖ The sample material is placed in a vacuum chamber at a constant and very low temperature, usually at the temperature of liquid nitrogen (77.4 K), and subjected to a wide range of pressures, to generate adsorption and desorption isotherms.
- ❖ The amounts of gas molecules adsorbed or desorbed are determined by the pressure variations due
- ❖ to the adsorption or desorption of the gas molecules by the material (the adsorbent).
- ❖ Various amounts of gas molecules will be adsorbed or desorbed at different doses of the gas (the adsorbate).
- ❖ Knowing the area occupied by one adsorbate molecule, (for example, $16.2 \text{ \AA}^2$ for nitrogen), and using an adsorption model, the total surface area of the material can be determined.
- ❖ The specific surface area that can be determined by gas sorption ranges from 0.01 to over $2000 \text{ m}^2 \text{ g}^{-1}$.
- ❖ Determination of pore size and pore size distribution of porous materials can also be made from the adsorption/desorption isotherm using an assessment model, suitable for the shape and structure of the pores. The range of pore sizes that can be measured using gas sorption is from a few Angstroms up to about half a micron.

4) Explain SEM method for characterization of nano materials?

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale.

This examination can yield information about the

- 1) Topography.
- 2) Morphology.
- 3) Composition and
- 4) Crystallographic information.

Electron Microscopes are mainly 2 types:

- 1) Transmission Electron Microscope (TEM) - allows one the study of the inner structures.
- 2) Scanning Electron Microscope (SEM) - used to visualize the surface of objects.

Principle of SEM:

Incoming (primary) electrons can be “reflected” (backscattered) from a bulk specimen and can release secondary electrons. Primary electrons are focused into a small- diameter electron probe that is scanned across the specimen. Electrostatic or magnetic fields, applied at right angles to the beam, can be used to change its direction of travel. By scanning simultaneously in two perpendicular directions, a square or rectangular area of specimen (known as a raster) can be covered. Image of this area can be formed by collecting secondary electrons from each point on the specimen.

Working of SEM:

- 1) The electron gun produces an electron beam when tungsten wire is heated by current.
- 2) This beam is accelerated by the anode.
- 3) The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample.
- 4) A mechanism of deflection coils enables to guide the beam so that it scans the surface of the sample in a rectangular frame.
- 5) When the beam touches the surface of the sample, it produces:
 - a) Secondary electrons (SE).
 - b) Back scattered electrons (BSE)
 - c) X - Rays.
- 6) The emitted SE is collected by SED and convert it into signal that is sent to a screen which produces final image.
- 7) Additional detectors collect these X-rays, BSE and produce corresponding images.
- 8) A secondary electron detector attracts the scattered electrons and, depending on the number of electrons that reach the detector, registers different levels of brightness on a monitor.
- 9) By reducing the size of the area scanned by the scan coils, the SEM changes the magnification of the image.

Advantages:

- 1) It gives detailed 3D and topographical imaging and the versatile information garnered from different detectors.
- 2) This instrument works very fast.
- 3) Modern SEMs allow for the generation of data in digital form.
- 4) Most SEM samples require minimal preparation actions.

Disadvantages:

- 1) SEMs are expensive and large.
- 2) Special training is required to operate an SEM.
- 3) The preparation of samples can result in artifacts.
- 4) SEMs are limited to solid samples.
- 5) SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.

5) Explain TEM method for characterization of nano materials?

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale.

This examination can yield information about the

- 1) Topography.
- 2) Morphology.
- 3) Composition and
- 4) Crystallographic information.

Electron Microscopes are mainly 2 types:

- 1) Transmission Electron Microscope (TEM) - allows one the study of the inner structures.
- 2) Scanning Electron Microscope (SEM) - used to visualize the surface of objects.

Principle of TEM:

Electrons possess a wave like character. Electrons emitted into vacuum from a heated filament with increased accelerating potential will have small wavelength. Such higher-energy electrons can penetrate distances of several microns into a solid. If these transmitted electrons could be focused then images are obtained with much better resolution. Focusing relies on the fact that, electrons also behave as negatively charged particles and are therefore deflected by electric or magnetic fields.

Working of TEM:

- 1) Specimen is bombarded by a beam of electrons, the primary electrons. The bombarding electrons are focussed to a bundle onto the object.
- 2) In areas in the object where these electrons encounter atoms with a heavy atomic nucleus, they rebound.
- 3) In regions where the material consists of lighter atoms, the electron are able to pass through.
- 4) The fine pattern of electrons leaving the object, reaches the objective lens forms the image.
- 5) It is then greatly enlarged by projector lens.
- 6) Eventually, the transmission electrons reach the scintillator plate at the base of the column of the microscope.
- 7) The scintillator contains phosphor compounds that can absorb the energy of the striking electrons and convert it to light flashes.
- 8) Thus a contrasted image is formed on this plate.

Advantages:

- 1) TEMs offer very powerful magnification and resolution.
- 2) TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields.

- 3) TEMs provide information on element and compound structure.
- 4) Images are high-quality and detailed.

Disadvantages:

- 1) TEMs are large and very expensive.
- 2) Operation and analysis requires special training.
- 3) Samples are limited to those that are electron transparent.
- 4) TEMs require special housing and maintenance.
- 5) Images are black and white .

6) Discuss the application of Nano materials in various fields.

In Industries:

1) As catalyst:

The nano materials have more no. of surface atoms which make them catalytically active. For example, bulk gold chemically inert while nano gold possess excellent catalytic property.

2) Water purification:

Dissolved salts and colour producing organic compounds can be filtered very easily from water by using nano porous membrane having pores smaller than 10nm. Magnetic nano particles are used to remove heavy metal contamination from waste water.

3) In Fabric industry: Embedding of Nano particles on fabrics make them stain repellent. Socks embedded with silver nano particles remove the bacteria and makes them odour free.

4) In automobiles:

Fuel consumption in automobiles can be reduced by using specially designed nano particles as fuel additives. Incorporation of small amount of nano particles in car bumpers make them stronger than steel

5) In food industry:

Nano particles are used to make packing material and containers to store food.

6) In Solar cells:

Absorption of solar radiation in solar cells containing nano particles are higher than the bulk materials.

In Medicine :

1) Nanodrugs:

Nano materials are used as drugs for the treatment of cancer and TB.

2) Nano medibots :

Nano particles act as nano medibots which identify and penetrate the cancer cells and destroy them by supplying anti cancer drugs

3) Gold coated Nano shells:

Gold coated nano shells containing silicon core are administered near the tumours . When IR light is irradiated on the skin externally, the gold nano shells absorb the light and convert in to heat which destroys the cancer cells responsible for tumour.

4) Gold nano particles as sensors:

Nano gold when mixed with different type microorganisms show different colours which is used to identify the harmless and dangerous micro organisms.

5) Protein analysis:

Gold nano particles injected in to the body reacts with the protein and the protein concentration can be detected by passing laser beam externally.

6) Gold nano shells for blood Immune assay:

Gold nano shells are used to detect WBC count in blood.

7) Gold nano shells in Imaging:

Gold nano shells is used as a scanning probe which gives the magnified image of cells in a body

8) Targetted drug delivery:

It involves slow and selective release of drug to the targeted organs.

In Electronics:

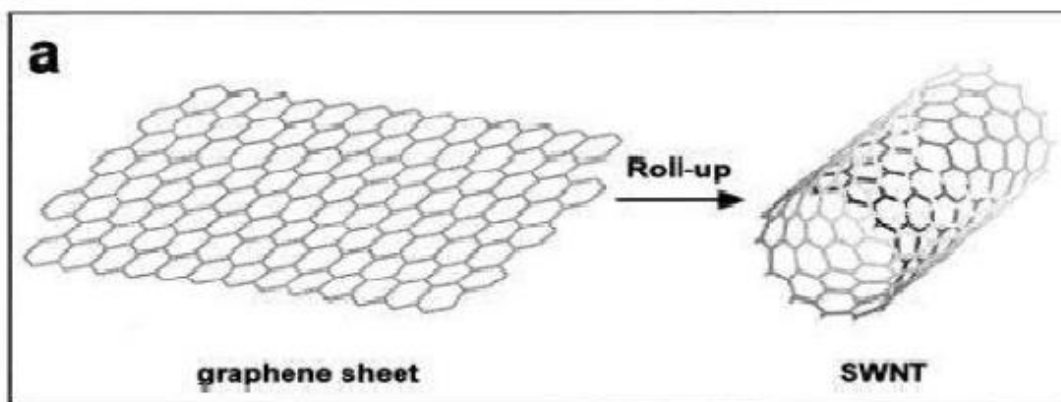
- 1) Quantum wires have electrical conductivity.
- 2) Nano radios are produced by using CNT.
- 3) MOSFET (Metal Oxide Semiconductor Field Effect Transistor) is used for Amplifying and switching electronic signals.
- 4) Nano wires are used to build transistors without p-n junction diode.
- 5) Transistor called NOMFET (Nano particle Organic Memory Field effect transistor) is created by combining Gold nano particles with organic molecules

Biomaterials:

- 1) Nano materials are used as bone cement and bone plates in hospitals
- 2) It is used as material for joint replacement
- 3) It is used in the manufacture of some components like heart valves, contact lenses, dental implants etc.

7) What are carbon nanotubes? Explain their classification.

Carbon NanoTubes (CNT): Carbon nanotubes are allotropes of carbon with a nanostructure having length to diameter ratio greater than 100,000. They are also called as Bucky tubes. These are long, thin cylinders of carbon, discovered by S. Iijima in 1991. They are considered as a sheet of graphite rolled into a cylinder. These have a broad range of electronic, thermal and structural properties depending on the length, diameter, chirality or twist of nanotube.



Rolling up a graphene sheet to form tubes:

Types of carbon nanotubes: Depending on the arrangement of atoms in carbon nanotubes, there are two types of carbon nanotubes.

- 1) Single walled nanotubes (SWNT)
- 2) Multi walled nanotubes (MWNT)

1) Single Walled Nano Tubes (SWNT):

- a) Single walled nanotubes have a diameter close to 1nm and run into million times longer than its diameter.
- b) They are obtained by wrapping a sheet of graphene (a single layer of graphite) into seamless sheets.
- c) There are three types of single walled nanotubes base on the way the graphene sheet is wrapped. Graphene sheet is represented by a pair of indices (n, m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in the honey comb crystal of graphene.
- d) If $m=0$, the nanotubes are zig-zig. The lines of the carbon bonds are down the centre.

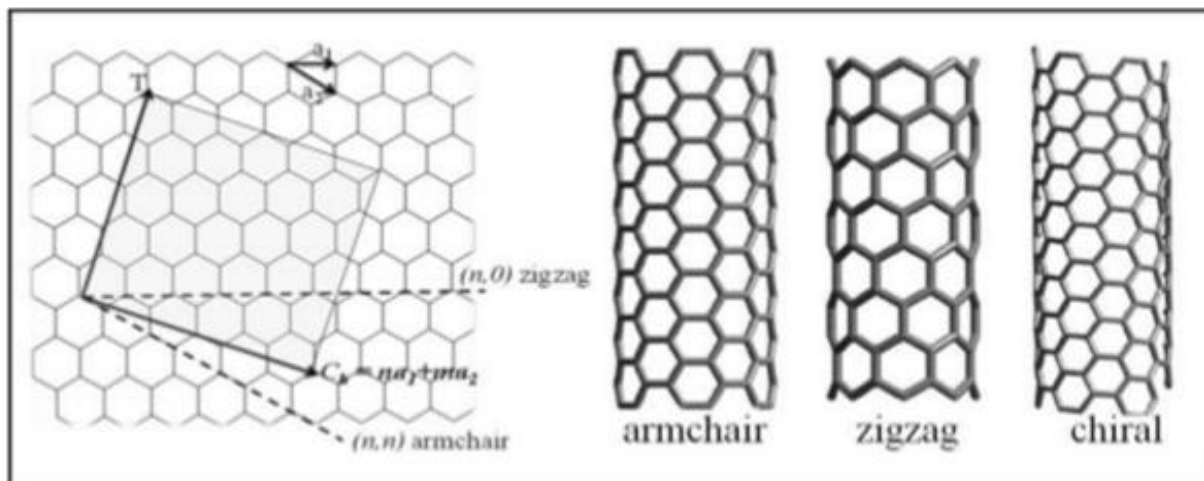
- e) If $n=m$, the nanotubes are called arm- chair. The lines of hexagons are parallel to the axis of the nanotubes.
- f) Otherwise, they are called ‘chiral’. They have a twist or spiral around the nanotubes.

2) Multi Walled Nano Tubes (MWNT):

Multi- walled nanotubes consist of multiple rolled concentric tubes of graphite. The interlayer distance in multi-walled nanotubes is close to the distance between grapheme layers. In graphite it is approximately 3.3Å.U. They have diameter close to 10 nm.

There are two models which can be used to describe the structures of multi-walled nanotubes

- a) In the Russian Doll model, sheets of graphite are arranged in concentric cylinders E.g:- A (0,8) single walled nanotube within a larger (0,10) Single – walled nanotube.
- b) In the Parchment model, a single sheet of graphite is rolled around itself, resembling a rolled newspaper.



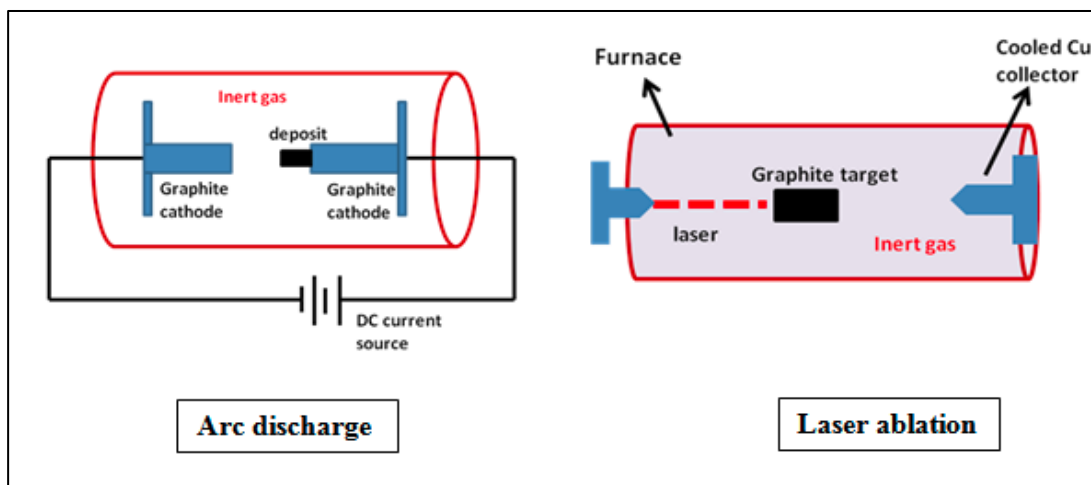
8) Discuss any TWO methods for preparation of carbon nanotubes.

Carbon nanotubes are generally prepared by three main techniques.

- 1) Arc discharge method.
- 2) Laser ablation method.
- 3) Chemical vapour deposition method.

1) Arc discharge method:

- a) It is the most common and easy method to prepare carbon nano tubes. (CNTs).
- b) This method uses high temperature electric discharge.
- c) Arc discharge method can be used to prepare both SWCNTs and MWCNTs.
- d) In this method two graphite rods are placed end to end, separated by approximately 1mm distance.
- e) These are placed in closed container filled with Helium gas to maintain inert atmosphere.
- f) The two graphite rods are connected to external battery.
- g) A direct current of 50 to 100A, produced from the battery creates a high temperature discharge between the two electrodes.
- h) This discharge vaporizes the surface of one of the graphite electrodes, and forms a small rod-shaped deposit on the other electrode.
- i) It is a technique that produces a complex mixture of components, and requires further purification- to separate the CNTs from the soot and the residual catalytic metals present in the crude product.

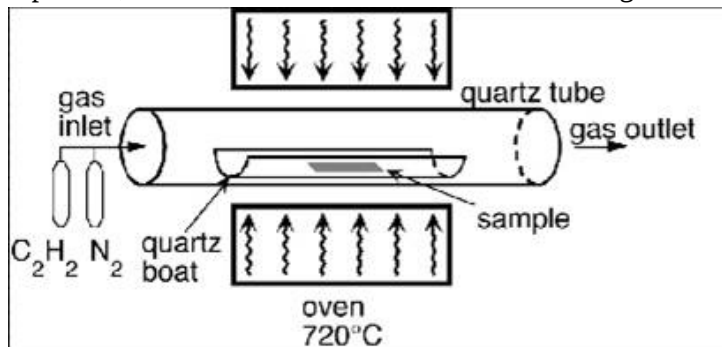


2) Laser ablation method:

- Laser Ablation method uses pulsed Laser to prepare CNTs.
- This method was developed by Smalley's group in the year 1996.
- In this method Graphite target is placed in Quartz tube surrounded by furnace maintained at a temperature of $1,200^{\circ}\text{C}$.
- Energy of the laser beam is focused on the graphite target.
- A pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas (argon) is passed into the chamber.
- Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses.
- A water-cooled copper collector may be included in the system to collect the nanotubes.
- The laser ablation method yields around 70%, and the purity of nanotubes is high.
- It is more expensive than either arc discharge or chemical vapour deposition methods.

3) Chemical Vapour deposition (CVD) method:

- In the chemical vapour deposition method carbon source is taken in gaseous form.
- In this method catalyst substrate is prepared with catalysts, most commonly used are nickel, cobalt, iron, or a combination.
- It is placed in quartz tube surrounded by hot oven maintained at 720°C .
- The substrate is heated in the tube.
- Now a carbon containing gas is passed in to the tube along with process gas.
- Carbon containing gas may be acetylene, ethylene, methane or ethanol etc. and Process gas used is ammonia, nitrogen or hydrogen.
- The carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. Nanotubes grow at the sites of the metal catalyst.



9) Describe the properties and applications of Carbon Nano Tubes [CNTs].

Carbon Nano Tubes [CNTs] have several unique chemical, optical, electrical and structural properties that make them attractive. The nano-materials possess very good catalytic activity due to increased area of contact. Due to edges and points, their catalytic activity is maximum. They exhibit good ability for easy dispersion. But CNTs possess toxicity and can cause harmful effects to vital organs with cell decay.

Properties of CNTs:

(1) Mechanical Properties:

Young's modulus of carbon nano tubes is 10 times greater than that of steel. CNTs have very structural defects in their walls, and hence, do not fracture on bending. The tensile strength of CNTs is about 20 times that of steel.

(2) Electrical Properties:

The electrical properties of CNTs vary between metallic to semiconducting materials. The very high electrical conductivity of CNT is due to the minimum defects in the structure.

(3) Thermal Conductivity:

The thermal conductivity of CNT is very high due to the vibration of covalent bonds due to minimum defects in the structure.

Due to the unusual and unique properties of CNTs they find potential **applications** in the following field:

- 1) Carbon nanotubes play an important role in the battery technology, because some charge carriers can be successfully stored inside the nanotubes.
- 2) Multi-walled CNTs can be used as storage devices to store hydrogen gas in fuel cells.
- 3) CNTs are used as catalyst in chemical reactions.
- 4) CNTs can be used for drug delivery within the body by placing the drugs within the tubes or by attaching the drug to the sides of the tubes.
- 5) CNTs are used as light weight shielding materials to protect electronic equipments from electromagnetic radiation.

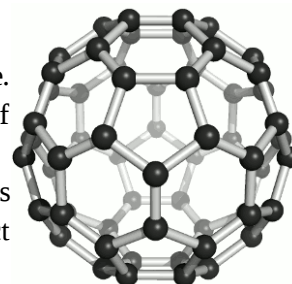
10) What are Fullerenes? How are they prepared? Explain their types.

Fullerenes are class of molecules made only carbon atoms having closed cage like structure. Fullerenes can be of a different type C 60, C 70, C 76, C 78, etc; depending on the number of carbon atoms.

The most important fullerene is C60 containing 60 carbon atoms which is commonly known as Buckminster fullerene, the name of Buckminster fullerene comes from the name of an architect Richard Buckminster fuller who had built the geodesic-dome with spherical shape.

The third newly discovered allotrope of carbon is Buck minister's fullerene during laser spectroscopy experiments. The structure of C60 resembles the geodesic dome (foot ball type).

Fullerenes can be made by vaporizing carbon With in a gas medium.



Preparation of fullerenes:

Fullerenes are prepared by vaporizing a graphite rod in He atmosphere when mixture of fullerenes formed are separated by multi step solvent extraction methods. C 60 is isolated by column chromatography using alumina/hexane solvent system.

Types of fullerenes:

A fullerene is any molecule entirely composed of carbon, in the form of hollow sphere, ellipsoid , tube or plane.

Thus fullerenes are of the following types:

- 1) Spherical fullerenes: They look like soccer (foot ball) ball and are often called bucky balls. Fullerenes are similar in structure to graphite composed of stacked graphene sheets, linked mostly of hexagonal or sometimes pentagonal / heptagonal rings. Buck minister's fullerene C60 is the simplest of all.
- 2) Cylindrical fullerenes: These are called carbon nanotubes or bucky tubes
- 3) Planar fullerenes: Graphene is an example of planar fullerene sheet.

11) Discuss the properties and applications of fullerenes?

Properties of fullerenes:

The bucky ball has cage like structure with certain unique properties. It is stable, denoted as C₆₀ and has sp² hybridized carbon atoms, whose reactivity is increased by attaching active groups on the surface. It exists as a discrete molecule. C₆₀ is a mustard coloured solid. When its thickness increases, it appears brown and then black. It is moderately soluble in the common organic solvents, especially aromatic hydrocarbons like toluene. It dissolves in benzene forming a deep magenta solution. It has a high tensile strength of any known 2D structure or element and has a high packing density. It can be compressed to 30% of its original volume, without destroying its cage structure. It is stable up to 600 °C and undergoes sublimation under vacuum at 600°C. It undergoes electrophilic addition at 6-6 double bonds. Other atoms can be trapped inside to form inclusion compounds.

Engineering applications of Fullerenes:

Fullerenes have amazing conducting, magnetic, optical and mechanical properties.

- 1) They can easily accept electrons, therefore, they may be used as charge carriers in batteries.
- 2) They can be used as organic photo voltaic cells as they have optical absorption properties.
- 3) Alkali metal fullerenes are super conductors.
- 4) They can be used as soft ferro-magnets.
- 5) Its spherical structure makes it suitable to be used as a lubricant.
- 6) Because of their extreme resilience and sturdy nature, fullerenes are used in manufacture of armor.
- 7) The water soluble derivatives inhibit the HIV-1 protease enzyme. They are useful in the treatment of HIV.
- 8) These are used as powerful anti-oxidants.
- 9) The fullerenes and fullerene black are chemically reactive and are added in the manufacture of copolymers with specific physical and mechanical properties.
- 10) They are used as catalysts as they have the ability to accept and transfer hydrogen atoms. They are highly effective in converting methane to higher hydrocarbons.

12) What are thermal analysis techniques.

Thermal analysis is a branch of material science where the properties of materials are studied as they change with temperature.

Some common methods are;

- 1)Thermo Gravimetric Analysis [TGA]
- 2)Differential Thermal Analysis [DTA]
- 3)Differential Scanning Calorimetry [DSC]

S.No.	Name of the technique	Instrument employed	Parameter measured	Graph
1	Thermo Gravimetric Analysis [TGA]	Thermobalance	Mass	Mass Vs Temperature
2	Differential Thermal Analysis [DTA]	DTA apparatus	Difference in temperature	ΔT Vs Temperature
3	Differential Scanning Calorimetry [DSC]	Calorimeter	Heat differences	dH/dt Vs Temperature

13) What is Thermo gravimetric analysis (TGA). Explain instrumentation and applications.

TGA is a technique in which the mass of a substance is measured as a function of temperature while a substance is subjected to a controlled temperature program.

Principle: In thermogravimetric analysis, the sample is heated in a given environment (air, N₂, CO₂, He, Ar, etc.) at controlled rate. The change in the weight of the substance is recorded as a function of temperature or time. The temperature is increased at a constant rate for a known initial weight of the substance and the changes in weights are recorded as a function of temperature at different time interval. This plot of weight change against temperature is called thermogravimetric curve or thermogram, this is the basic principle of TGA.

Instrumentation of TGA :

The apparatus required for TGA analysis are;

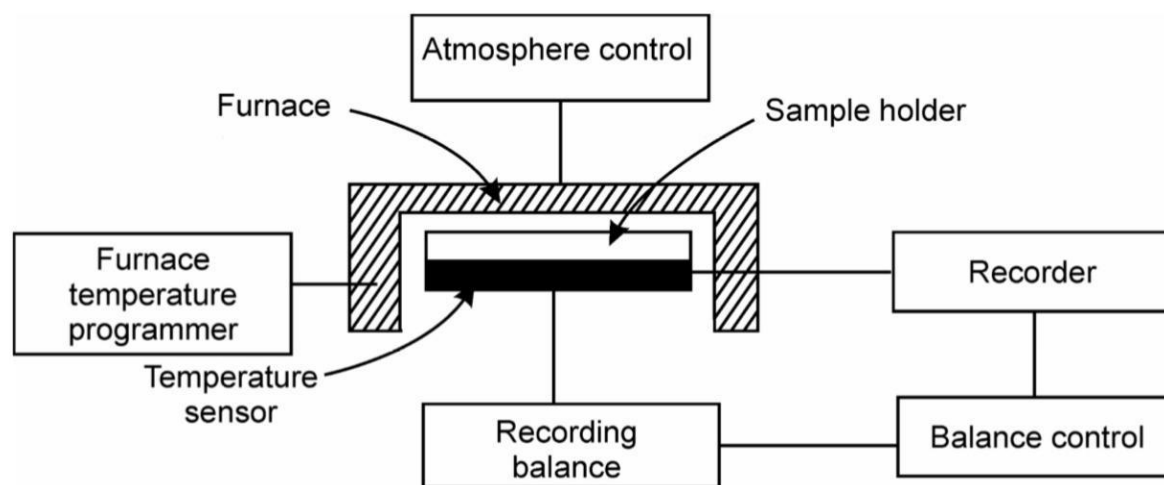
(a) A furnace which can be heated so that the temperature gives linearity with time.

(b) A furnace controlled thermobalance

(c) A known weight of the sample is taken in a crucible which is enclosed by a furnace(F).

The furnace(F) temperature is raised slowly, the temperature of the sample and the corresponding weight are taken. A platinum/platinum rhodium thermocouple is used to measure the sample temperature, and the change in weights are found out by finding the beam deflection on adding a known weight to the pan.(i.e) the change in the weight are recorded from the beam deflection.

A recorder records the change in weight in y axis and w.r.to temperature on the x-axis. We get a thermogram.



Applications of TGA:

- 1) From TGA, we can determine the purity and thermal stability of both primary and secondary standard.
- 2) Determination of the composition of complex mixture and decomposition of complex.
- 3) For studying the sublimation behaviour of various substances.
- 4) TGA is used to study the kinetics of the reaction rate constant.
- 5) TGA can be used as a technique to characterise materials used in various environmental, food , pharmaceutical & petrochemical applications.
- 6) Used in the study of catalyst: The change in the chemical states of the catalyst may be studied by TGA techniques. (Zn-ZnCrO₄) Zinc-Zinc chromate is used as the catalyst in the synthesis of methanol.

14) What is Differential Thermal analysis (DTA). Explain instrumentation and applications.

DTA is a technique in which the temperature between sample and thermally inert reference substance is continuously recorded as a function of temperature.

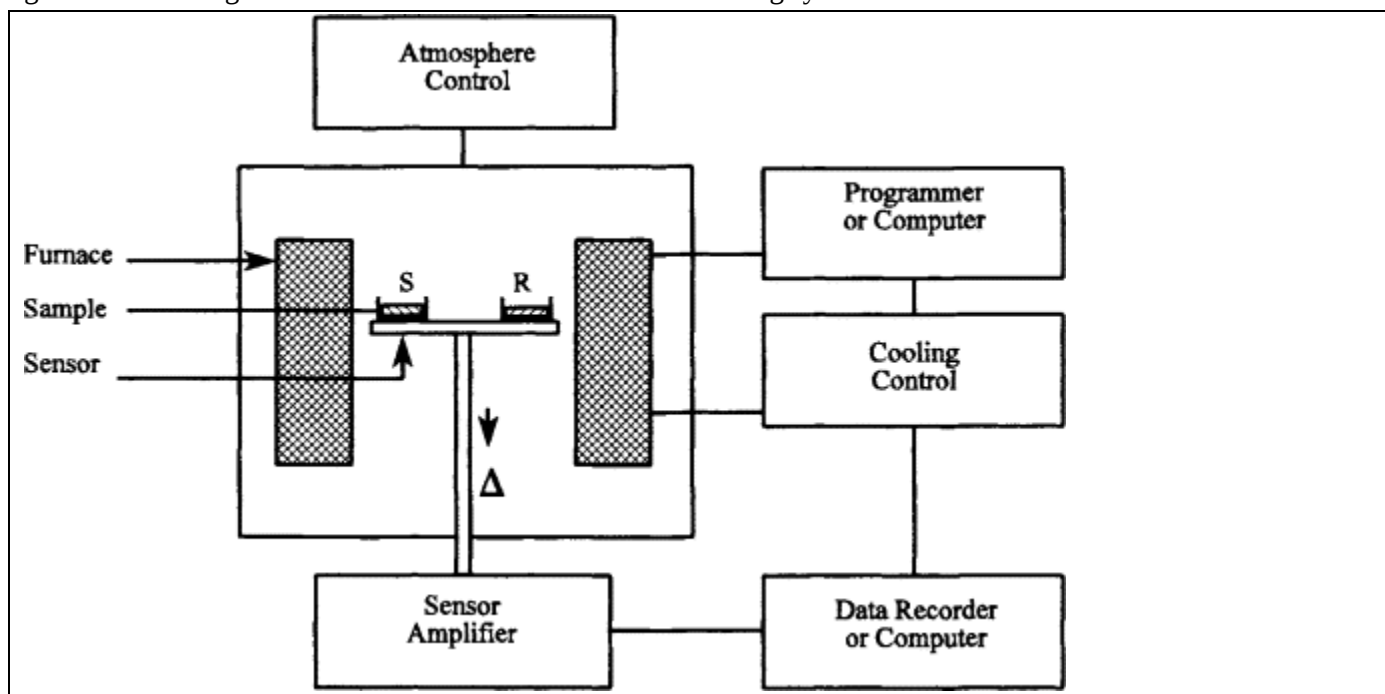
Principle: DTA is a technique in which the temperature of the substance under investigation is compared with the temperature of a thermally inert material. This differential temperature is then plotted against time or against temperature. If zero temperature difference between sample and reference material, sample does not undergo any chemical or physical change. If any reaction takes place temperature difference will occur between sample and

reference material.

Instrumentation:

The apparatus consists of a) Sample holder b) Furnace c) Sensors and Recording system.

The sample holder contains two crucibles one for the sample and second one for the reference. The dimensions of the two crucibles should be nearly identical. The weights of the sample and the reference should be virtually equal. The sample and reference should be matched thermally and arranged symmetrically with the furnace so that they are both heated or cooled in an identical manner. The temperature difference between the sample and reference generates a net signal which is recorded in sensors and recording system.



Applications of DTA:

- 1) Using DTA, we can detect the decomposition of the sample.
- 2) Using DTA, we can detect the volatilisation of the sample.
- 3) The main use of DTA is to detect thermal processes and characterise them as exothermic or endothermic, reversible or irreversible.
- 4) DTA thermal curves can be used to determine the order of a reaction.
- 5) DTA method can be used to measure crystallisation, melting points, changes in solid crystal phases.
- 6) DTA is widely used in the pharmaceuticals and food industries.
- 7) DTA may be used in cement chemistry, mineralogical research and in environmental studies.

15) Explain the instrumentation and applications of Differential scanning calorimetry.

DSC is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as function of temperature.

Principle: When a sample undergoes a physical transformation such as a phase transition more or less heat will need to flow to it than to the reference to maintain both at the same temperature whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic.

Instrumentation:

There are two different types of DSC instruments 1) Heat flux DSC 2) Power compensated DSC.

1) Heat flux DSC:

In heat flux DSC the difference in heat flow into the sample and reference is measured while the sample temperature is changed at the constant rate.

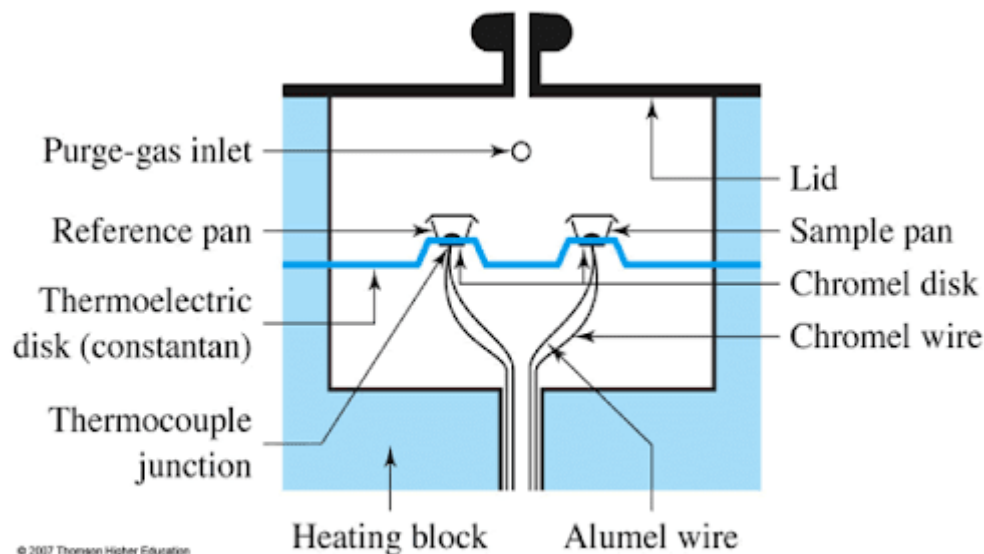


Figure 1: Heat Flux DSC

DSC apparatus is enclosed in a heating block.

The heat is transferred to the sample with the help of thermoelectric disk (or) constantan.

The disk has two raised platforms on which the sample and reference pans are placed.

A chromel disk and connecting wire are attached to the underside of each platform and the resulting chromel-constantan thermocouples are used to determine the differential temperatures of interest.

Alumel wires attached to the chrome discs provide the chromel – alumel junctions for independently measuring the sample and reference temperature.

In heat flux DSC, we can write the total heat flow dH/dt as ,

$$dH/dt = C_p dT/dt + f(T,t)$$

Where, H = enthalpy in J/mol

C_p = Specific heat capacity in J/K/mole

$f(T,t)$ = Kinetic response of the sample in J/mol

Thus the total heat flow is the sum of the two terms one related to the heat capacity and one related to the kinetic response.

2)Power compensated DSC:

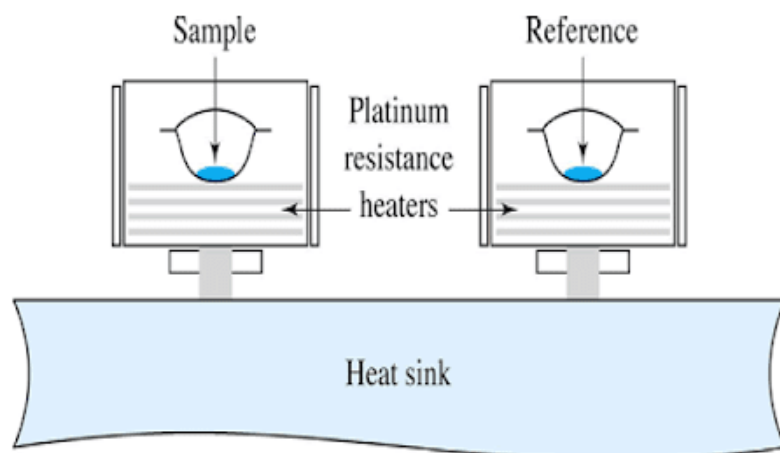


Figure 6: power compensation DSC

In power compensation DSC the temperature of the sample and reference are kept equal to each other while both

temperatures are increased or decreased linearly.

The power needed to maintain the sample temperature equal to the reference temperature is measured.

In power compensation DSC two independent heating units are employed.

The heating units are embedded in a large temperature –controlled heat sink.

The sample and reference holders have platinum resistance thermometers to continuously monitor the temperature of the materials.

The instrument records the power difference needed to maintain the sample and reference at the same temperature as a function of the programmed temperatures.

Applications of DSC:

- 1) Determination of heat capacity.
- 2) Determination of glass transition temperature.
- 3) Determination of temperature of crystallisation.
- 4) Determination of Metal alloy melting temperatures and heat of fusion.
- 5) Determination of melting behaviour of complex organic materials.
- 6) Identification of an unknown material.
- 7) Determination of crystalline to amorphous transition temperatures in polymers and plastics.

PART - B

16) Define Refractories. Give the classification of refractories with suitable examples.

Refractories:- A substance that is difficult to fuse is called a refractory. A refractory is a material which does not melt easily and its fusion temperature is very high. They are inorganic materials which can withstand high temperatures, abrasive and corrosive actions without any deformation in shape.

Classification:- **Based on fusion temperature**, they are of 3 types:

- Normal refractories:- They have fusion temperature in the range of 1580-1780 °C. Eg:- fire clay.
- High refractories:- They have fusion temperature in the range of 1780-2000 °C. Eg:- chromite.
- Super refractories:- They have fusion temperature in the range of about 2000 °C. Eg:- zircon.

Classification:- **Based on chemical composition**, they are of 3 types:

- Acidic refractories:- They consist of acidic materials like alumina and silica. These refractory materials are resistant to acid slags and are readily attacked by basic slags.
Eg:- Alumina, silica and fire clay refractories.
- Basic refractories:- They consist of basic materials like CaO, MgO etc. and are resistant to basic slags. They are widely used in steel making open hearth furnaces.
Eg:- magnesite and dolomite bricks.
- Neutral refractories:- They are made from weakly basic or acidic materials like carbon, zirconia and chromite. Neutral refractories show resistance to the action of basic and acidic materials. They show good chemical stability.
Eg:- graphite, zirconia and carborundum.

Classification:- **Based on oxide content**, the refractories are classified into 3 types:

- Single oxide refractories:- Eg:- alumina, magnesia and zirconia.
- Mixed oxide refractories:- Eg:- zircon, spinel.
- Non oxide refractories:- Eg:- Borides, carbides, silicides etc.

17) Write short notes on properties of refractories.

- 1) Refractoriness.
- 2) RUL. [Refractoriness Under Load]
- 3) Porosity.
- 4) Thermal spalling.
- 5) Dimensional stability.
- 6) Thermal conductivity.

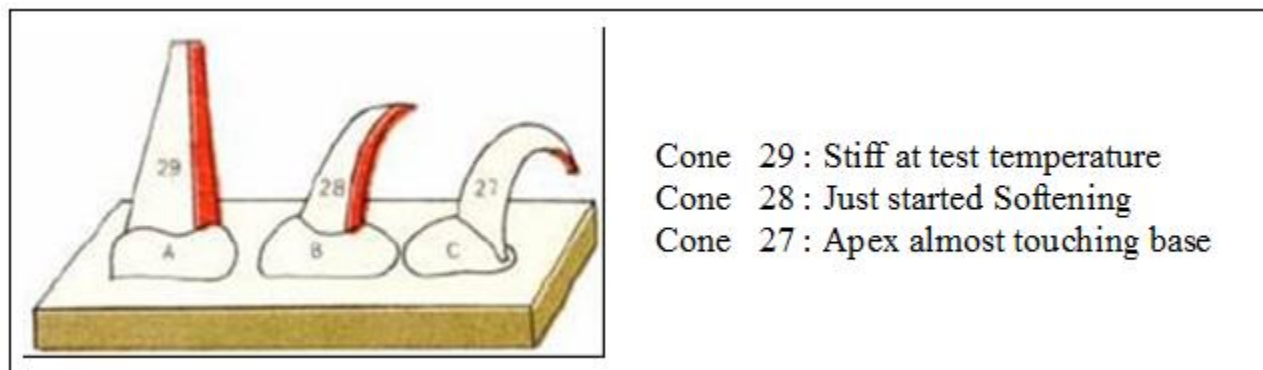
1) Refractoriness:-

- It is the ability of a material to withstand high temperature without deformation under working conditions.
- It is the softening temperature of the material.
- Higher the softening temperature, more valuable is the refractory.
- The prime function of a refractory is to withstand high temperatures.
- So its softening temperature should be above the operating temperature.

Measurement of refractoriness:

It is determined by pyrometric cone or segar cone test. The test refractory in the form of a cone (38 mm height & 19 mm base) is kept along with similar sized standard cones. They are heated uniformly at 100°C per minute. Each standard cone is made of a particular refractory with a definite softening temperature. These standard cones are assigned

certain numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard cones whose softening temperature is close to the test cone will also soften. The serial number of this standard cone will be the Pyrometric cone equivalent (PCE) of the test cone. If the test cone softens earlier than one and latter than next, the PCE value of the test cone is measured as the average of the two.



Temperature at which the refractory brick or the cone bends (i.e.) the temperature at which apex touches the base is called refractoriness (units PCE). Refractory cannot be used above this temperature.

Some examples are given in the table.

Refractory	PCE numbers	Softening temperature
Silica bricks	32	1710 °C
Alumina bricks	36-38	1800-1850 °C
Magnesite bricks	38	1850 °C

2) Refractoriness Under Load: (RUL):

The temperature at which the refractory deforms by 10 % is called refractoriness under load. (i.e.) The load bearing capacity of a refractory can be measured by RUL test.

- i) A good refractory should have high RUL value.
- ii) Refractoriness determines the strength of a refractory.
- iii) The essential qualities of a refractory are temperature resistance and load bearing capacity.
- iv) The refractory lined furnaces are generally charged with heavy reactants.
- v) So they should with stand heavy loads at high temperatures.

Eg:- Fire clay refractories collapse at temperatures below their fusion temperatures when heavy load is applied. Silica refractories with stand loads even at high temperatures.

RUL test is performed to know the safe upper temperature limit up to which the refractory can be used. The RUL test is done in rectangular container by applying a load of 75 kg/cm² on to the refractory and heating at a constant rate of 10°C per minute. During this process, the specimen will soften and its height will decrease under the load. This decrease in height is measured and when there is 10% decrease to that of original height, the temperature is noted. The RUL is then expressed as the temperature at which this 10% deformation occurs.

3) Porosity: It is defined as the ratio of pore volume to the bulk volume.

$$P = (W - D / W - A) \times 100$$

W – weight of saturated specimen in air

D – weight of dry specimen

A – weight of saturated specimen in water

It is the measure of number of pores incorporated during the manufacture of refractory bricks.

Porosity reduces strength, corrosion resistance, thermal conductivity, thermal spalling and abrasion resistance.

4) Thermal spalling: It is the property of breaking, cracking or peeling of refractory material under high temperature. Thermal spalling may be due to rapid change in temperature or slag penetration. A good refractory should show good resistance to thermal spalling.

Spalling can be minimised by:

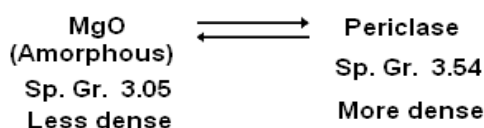
- Avoiding sudden fluctuations in temperature.
- Proper selection of refractory material with high thermal conductivity, uniformity and high porosity.
- by over firing the refractory materials.
- improved furnace design to minimise stress and strain during operation.

5) Dimensional stability (Thermal expansion & contraction):

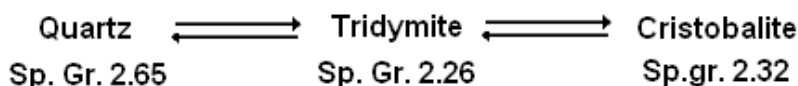
The resistance of refractory material to any change in volume due to exposure to high temperature is known as its dimensional stability. Refractories may undergo reversible or irreversible dimensional changes. Irreversible or permanent changes may be due to contraction or expansion of brick material

A good refractory should show minimum level of reversible dimensional changes with temperature.

Examples: Some materials like magnesite, chrome magnesite, fire brick shrinkage due to transformation of one crystalline form to another.



Some materials like silica bricks undergo phase transformations.



6) Thermal conductivity:-

In the industrial applications, refractory materials of both high and low thermal conductivity are required depending on the type of furnace. The conductivity of a refractory depends on its chemical composition and porosity. As porosity increases the thermal conductivity decreases because the entrapped air in the pore functions as insulator. Dense refractories have high thermal conductivity.

Most of the furnaces are lined inside with refractory material of low thermal conductivity to reduce heat loss to outside. Eg: fireclay & silica. In muffle furnaces, construction of retorts, the heat should be transmitted. So carbon and silicon carbide refractories which are poor conductors are used.

18) What are the causes of failure of refractories?

The refractory material failure may be caused by many different factors, such as chemical reaction and corrosion, spalling, material selection, plant operations, material storage, mixing, installation, curing, and drying.

1) Chemical reaction and corrosion:

The most common cause for failure of refractory is chemical reaction with the environment in which it is operating and chemical corrosion from molten slag and hot gas/molten salt. Chemical corrosion of a refractory is caused by slag attack at the refractory surface. The material selected must match the chemical environment that exists.

For example, an acidic refractory should not be used in furnaces using basic fluxes, slag, etc. and vice-versa.

The porosity of refractory plays an important role in the chemical reaction. The more porous it is, the greater will be the depth to which the slag will penetrate and destroy the refractory. Sometimes, rise in temperature beyond the safe limit quickly brings about the destruction of the refractory.

2) Spalling:

Another important cause is spalling. It may be thermal, mechanical or structural.

Thermal spalling may be due to unequal expansion or contraction caused by the difference in temperature at different parts.

Mechanical spalling is mostly due to carelessness in loading the furnace or in the removal of materials from furnace, thereby damaging the refractory.

Structural spalling takes place due to change in composition of the refractory because of reaction with slags, flux, etc. as a result its coefficient of expansion changes. Thus, different parts expand and contract to a different extent.

3) Improper material storage, mixing, installation, curing and drying:

Improper material storage, mixing, installation, curing and drying will also cause refractory failure. Refractory material should always be stored in dry, well-ventilated conditions. Use fresh refractory materials and follow proper storage procedures to ensure that the refractory will not lose strength. Use potable water (suitable for drinking) for mixing. The use of the wrong type of water will hinder the ability of the refractory material to reach its proper strength. Using the right type of mixer, following proper mixing procedures, and staying within recommended pot life are other important installation factors. Using the wrong mixer or pneumatic gun could also affect the strength of the refractory material. Almost all refractory materials (except those that are phosphate bonded) must be cured prior to the drying process. Failure to properly cure a cement-bonded refractory material is the number one contributor to refractory failure and lack of longevity.

4) Quality of the refractory material:

Problems with the quality of the refractory material itself is also an important reason for the failure of refractories. A selection of the right refractories for a specific application is important.

19) Define lubricant? What are the functions of a good lubricants.

Def: Lubricant is a substance used in between two moving surfaces to reduce the friction. Lubrication is a process of reducing friction and wear between two moving surfaces by adding lubricant in between them.

Criteria of a good lubricant:- A good lubricant must have the following functions:

- 1) The first and foremost function is to reduce friction.
- 2) It reduces surface deformation, wear and tear because the direct contact between the rubbing surfaces is avoided.
- 3) It reduces waste of energy. Hence the efficiency of the machine is enhanced.
- 4) It reduces expansion of metal by local frictional heat.
- 5) It avoids seizure of moving surfaces as the lubricant minimises the liberation of frictional heat.
- 6) It avoids unsmooth relative motion of moving parts.
- 7) It reduces the maintenance and running cost of machine, by preventing rust and corrosion.
- 8) It also acts as a seal.

20) Discuss the Classification of Lubricants?

Classification of Lubricants: Lubricants may be broadly classified as follows:

- 1) Solid lubricants : Eg:(a) Graphite, (b) Molybdenum disulphide , (c) Talc, (d) Mica.
- 2) Semi – solid Lubricants: (a) Greases (b) Vaseline's
- 3) Liquid lubricants:
 - (a) Vegetable oils – eg: palm oil & castor oil
 - (b) Animal oils - eg: Whale oil & lard oil
 - (c) Mineral oils – eg: petroleum fractions.
 - (d) Blended or compounded oils: Eg:Mineral oils with various additives to induce desired properties.
 - (e) Synthetic oils – eg: Silicones.

21) Explain the different theories of the mechanism of lubrication.

Mechanism of lubrication:-

There are mainly three types of mechanisms by which lubrication takes place. They are:

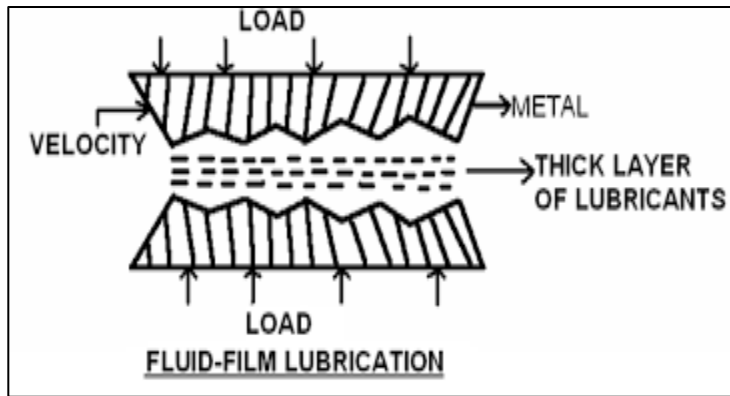
- 1) Fluid-film lubrication (Thick-film lubrication).
- 2) Boundary lubrication (Thin-film lubrication).
- 3) Extreme pressure lubrication.

1) Fluid-film lubrication:

It is known as thick film lubrication or hydrodynamic lubrication. It is done by lubricants which are liquid in nature. The thickness of lubricants in this case is about 1000 Å, hence the name 'Thick-Film lubrication'

In this type of lubrication, the moving or sliding surfaces are separated from each other by a thick film of fluid, so that there is no direct contact between them. The lubricant film covers the irregularities of the surfaces and reduces friction and wear and tear. The resistance to movement of sliding or moving parts is due to internal resistance between the particles of the lubricant moving over each other. For this, the lubricant should have minimum viscosity under working conditions. It should remain in place and separate the surfaces.

This type of lubrication is used in delicate and light machines like watches, clocks, guns, sewing machines and in heavy machines like turbines, submarines etc. Fluid film lubrication is satisfactory done by hydrocarbon oils. Hydrocarbon oils used are generally mixed with long chain polymers in order to maintain the viscosity of the oil constant in all the season of the year.



2) Boundary lubrication: (Thin-film lubrication):

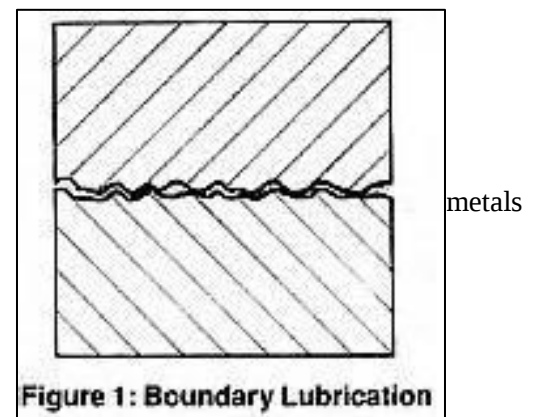
It is also known as thin-film lubrication because the thickness of the lubricant used in this type may not exceed one or two molecular layers. Boundary lubrication is necessary when fluid film lubrication fails to maintain the lubrication.

This type of lubrication occurs when a continuous film of lubricant cannot persist and direct metal to metal is possible. In these conditions, the space between the moving or sliding surfaces is lubricated so that a thin layer of lubricant is adsorbed on the metallic surfaces due to physical or chemical forces. This adsorbed layer helps to avoid the direct metal to metal contact between the rubbing surfaces. This load is carried by the layers of adsorbed lubricant on both the metal surfaces.

The coefficient of friction varies from 0.05 to 0.15.

For boundary lubrication, the lubricant molecules should have;

1. Long hydrocarbon chains.
2. Polar groups to promote wetting or spreading over the surface.
3. Lateral attraction between the chains.
4. Active functional groups which can form chemical bonds with or other surfaces.
5. High viscosity index,
6. Good oiliness,
7. Resistance to heat and oxidation.



Solid lubricants, greases and oils with proper additives function as lubricants in this type of lubrication. For example, graphite, molybdenum disulphide, mineral oils with additives of fatty acids or fatty oils, vegetable and animal oils and their soaps. These materials form films on the metal surfaces having internal friction. So they can bear compression and high temperatures.

3) Extreme Pressure lubrication:

When the moving or sliding surfaces are under high pressure and speed, a special type of lubricants is used called high pressure lubricants. They withstand high temperatures generated due to friction. When moving surfaces are working under

very high temperature and pressure, the ordinary liquid lubricants either vaporises or decomposes. In such cases, extreme pressure lubrication is done.

For this, special additives are used along with the liquid lubricants. Chlorinated esters, sulphurized oils and tricrysl phosphates are some examples. These additive compounds combine with the metallic surfaces at high temperatures and form metallic chlorides, sulphides or phosphides in the form of a durable film. These films can withstand very high loads and temperatures due to their high melting point.

Extreme pressure lubricants have great advantages:

- i) They are used in wire drawing machining of tough metals etc.
- ii) In cutting fluids in machining of tough metals.

21) Write short notes on the following properties of lubricants: (a) Cloud and Pour point (b) Flash and Fire point. (c) Viscosity and Viscosity index. d) Aniline point.

The properties of lubricants:

- 1. Viscosity
- 2. Viscosity Index
- 3. Flash and Fire Point
- 4. Cloud and Pour Point
- 5. Oiliness.
- 6. Aniline point.

1.Viscosity:

Viscosity of lubricating oil is the property which creates internal resistance to its flows. Good lubricating oil should always have moderate viscosity. Lower the viscosity, greater the flow ability. If the viscosity of the lubricating oil is high, then restriction of moving or sliding parts of a machine will occur leading to wear and tear. Lubricating oil with low viscosity will not be able to form a film and it will be squeezed out of the machine leading to a friction.

Viscosity of oil can be determined with the help of red wood viscometer or sayboltz viscometer. Viscosity of oil is inversely proportional to its temperature.

Significance:

Viscosity helps in the selection of good lubricating oil. Viscosity helps in the selection of good lubricating oil. Light oils have low densities and easy flow abilities and are used on parts moving a high speed. Heavy oils are used on parts moving at slow speed under heavy loads.

2.Viscosity Index (V.I)

It is the rate of change of viscosity of oil with temperature . It is also called as viscosity temperature curves.

The viscosity of a good lubricating oil should not change much with change in temperature. But in general, for every 1 °C rise in temperature, the viscosity index decreases by 2%

3.Flash and Fire Point:

Flash point: It is the minimum temperature at which the lubricating oil produces enough vapor to ignite for a moment when the flame is brought near it.

Fire point: It is the minimum temperature at which the vapors of the lubricating oil burn continuously for 5 seconds when a tiny flame is brought near it.

Significance: flash and fire point determination helps in identifying a type of lubricant for particular machinery.

4.Cloud And Pour Point:

Cloud Point: It is the temperature at which the lubricating oil become cloudy in appearance when it is cooled slowly.

Pour Point: It is the temperature at which the lubricating oil stops to flow.

Significance: Cloud and pour point determination helps in identifying lubricating oil, which can be used in cold conditions.

5. Oiliness: It is the measure of an ability of a lubricant to stick to the surface of moving or sliding parts of a machine under heavy load and high pressure. Lubricant with high oiliness: vegetable and animal oil.
Lubricant with low oiliness: mineral oil.

Significance: always a good lubricant should have high oiliness.

6. Aniline point: The aniline point of an oil is defined as the minimum temperature at which equal volumes of aniline ($C_6H_5NH_2$) and the lubricant oil are miscible, i.e. form a single phase upon mixing..

The value gives an approximation for the content of aromatic compounds in the oil, since the miscibility of aniline, which is also an aromatic compound suggests the presence of similar (i.e. aromatic) compounds in the oil. The lower the aniline point, the greater is the content of aromatic compounds in the oil.

22) Write a brief account on constituents of cement.

Cement: Concrete is most widely used non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is the essential bonding material which binds sand and rock when mixed with water.

Cement is classified into two types, based on its nature.

1. **hydraulic cement:** It is capable of setting and hardening in the presence of water. Eg. Portland cement.
2. **non-hydraulic cement:** These harden in air and cannot be used under water. Eg. Lime gypsum, plaster of paris etc.

Constituents of cement (compound composition):

The raw materials used in the manufacture of cement, combine during the process to form the compound. The quality of cement depends on the composition of the compound.

Clinker	CCN (Notation)	Mass %
Tri calcium silicate $3CaO \cdot SiO_2$	C_3S	75%
Di calcium silicate $2CaO \cdot SiO_2$	C_2S	7 – 32%
Tri calcium aluminate $3CaO \cdot Al_2O_3$	C_3A	0 – 13%
Tetra calcium aluminoferrite $4CaO \cdot SiO_2 \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	0 – 18%
Gypsum $CaSO_4 \cdot 2H_2O$	-----	2 – 10%

23) Explain the manufacturing of Portland cement by rotary kiln method? (or) Preparation of cement.

Manufacture of Portland cement by rotary kiln:

Portland cement is the most common type of cement which is in use around the world. Joseph Asphidin first prepared Portland from lime stone and clay. Later his son improved the quality of cement.

Raw materials:

1. Calcareous materials, CaO [such as limestone, chalk, marble etc.].

2. Argillaceous materials, Al_2O_3 and SiO_2 [such as clay, slate, shale etc.].
3. Powdered Coal or fuel oil and
4. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Various stages in the manufacture of cement:

1) Mixing of raw materials:

The properly ground raw materials are mixed either by dry process or wet process.

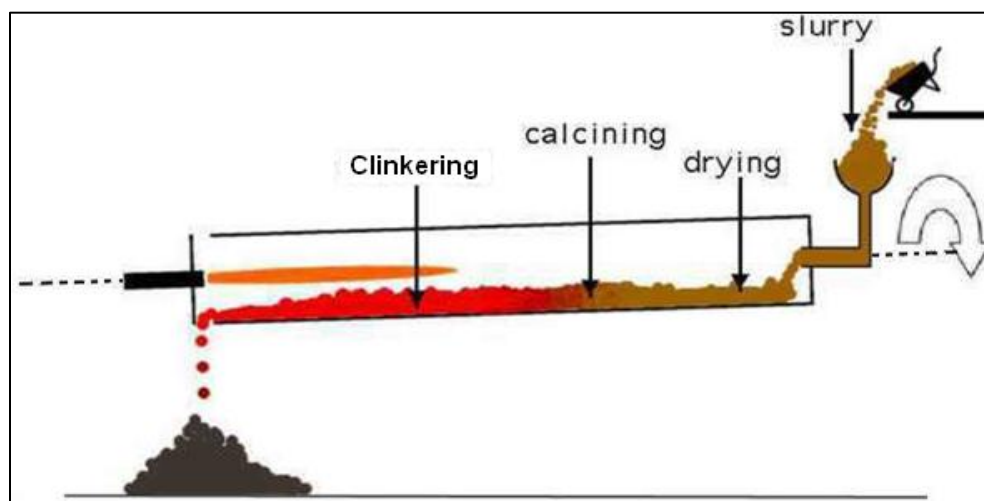
Dry process:

- ☒ This process is used for the raw materials are quite hard (cement rock or slag).
- ☒ The raw materials are crushed and ground separately to a fine powder.
- ☒ Each of these is separately stored in a separate hopper.
- ☒ The two are then mixed in required proportions to form a raw mixture which is stored in bins.

Wet process:

- ☒ In this process, the raw materials are crushed and ground to particles of suitable size and then mixed with 30 – 40% water to make it slurry by using compressed air.
- ☒ The slurry is pumped to correction basin where its composition is adjusted.
- ☒ The slurry is stored in storage tanks.
- ☒ By this method, the composition can be easily controlled.
- ☒ But this process requires more energy (fuel) than dry process since water used has to be removed.

Dry process	Wet process
✓ Slow process ✓ Cost of production is less ✓ Inferior quality cement is produced ✓ This is meant for hard materials. ✓ Shorter kiln is sufficient	✓ Relatively fast process ✓ Cost of production is more ✓ Superior quality cement is produced ✓ This is meant for soft materials. ✓ Longer kiln is required.



2) Calcination.(burning) :

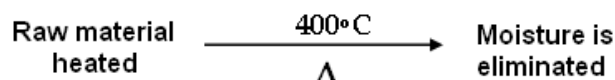
Rotatory kiln consists of a long horizontal steel cylinder, lined with Refractories and rotating at the speed of 0.5 – 2 RPM. The dimensions of the steel cylinder vary with the quantity of production. The kiln is slightly inclined at the angle of 3 – 6°. The inclination allows the material fed in the upper end to travel slowly to the other end.

Process: The ‘raw-mix’ is injected into the kiln at the upper end; while a hot flame is forced into the kiln from the lower end. Due to the slope and slow rotation of the kiln, the material fed move continuously towards the hottest-end at a speed of about 15m per hour. As the slurry gradually descends down the kiln due to rotation, the temperature rises.

There are **3 zones** in the kiln where the material undergoes various chemical changes.

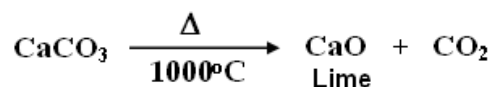
a) Drying Zone:

It is the upper part of the kiln, the temperature of which is around 400 °C. Here most of the water in slurry gets evaporated.



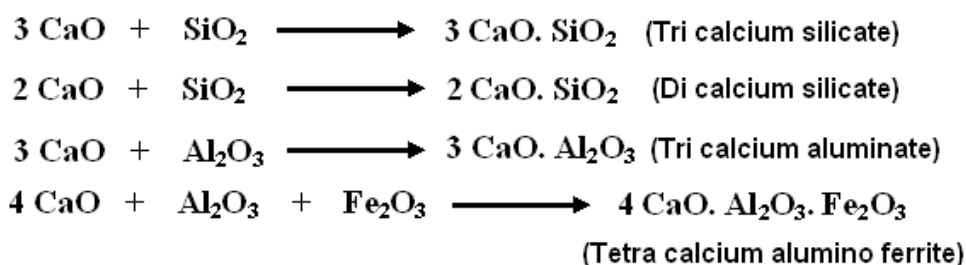
b) Calcination Zone:

It is the central part of the kiln, where the temperature is around 1000 °C. Here the limestone or dry mix or slurry undergoes decomposition to form quicklime and carbon dioxide. The material forms small lumps called nodules.



c) Clinkering Zone:

It is the lower part of the kiln, where the temperature is 1500 °C to 1700 °C. Here lime and clay undergo chemical interaction yielding calcium aluminates and silicates.



The aluminates and silicates of calcium fuse together to form small, hard, greyish stones, known as clinkers. These are very hot and are at about 1000 °C. The rotary kiln is supported with small kiln, used to cool the clinkers by air-counter blast. This hot-air is further used for burning powdered coal/oil left if any.

3) Mixing of clinkers of cement with gypsum:

The cooled clinkers are collected from cooling cylinders at the bottom of the kiln and are ground to a fine powder in ball mills. During final grounding, a small quantity (2.3%) of powdered gypsum is added, so that the resulting cement does not set quickly, when it comes into contact with water or moisture. Gypsum retards the early setting of cement. After the

initial set, the cement water paste become stiff, but the gypsum retards the dissolution of C 3 A by forming tricalcium sulphoaluminate. The insoluble tricalcium sulphoaluminate prevents too early further reactions of setting and hardening.

4. Packing:

The ground cement is stored in silos, from which it is fed to automatic packing machines. Each bag contains 50Kg of cement.

24) Explain with equations Setting and hardening of cement? (or) Write a brief account on setting and hardening of cement?

Setting and Hardening of cement:-

Cement when mixed with water forms a plastic mass called cement paste. During hydration reaction, gel and crystalline products are formed. The inter-locking of the crystals binds the inert particles of the aggregates into a compact rock like material.

This process of solidification comprises of

(i) setting and then

(ii) hardening.

Setting: Setting is defined as stiffening of the original plastic mass due to initial gel formation.

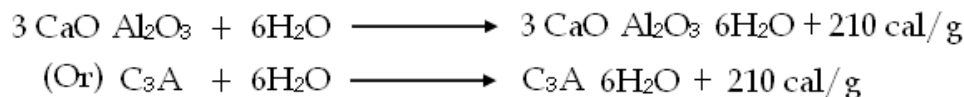
Hardening: Hardening is development of strength, due to crystallisation. Solidification of stiffened mass to form a rock like material is known as hardening.

Mostly setting requires 24 hours where as hardening requires 15 – 20 days. The setting and hardening of cement is due to hydration and hydrolysis of its constituents.

Due to the gradual progress of crystallisation in the interior mass of cement, hardening starts after setting. The strength developed by cement paste at any time depends upon the amount of gel formed and the extent of crystallisation. The setting and hardening of cement is due to the formation of inter locking crystals reinforced by rigid gels formed by the hydration and hydrolysis of the constitutional compounds.

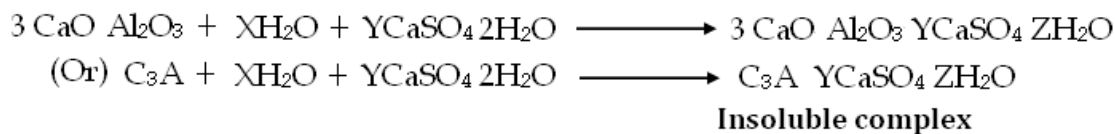
Chemical reactions involved in setting and hardening of cement:

When the cement is mixed with water, the paste so formed becomes stiff due to hydration of tri calcium aluminate (C_3A).

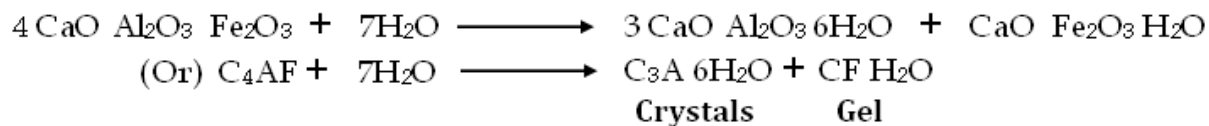


- This type of hydration is not desirable because it does not allow hydration of other constituents.
- It is delayed by adding gypsum.

✓ Gypsum reacts with C_3A to form insoluble complex calcium sulfo aluminate which does not hydrate rapidly.

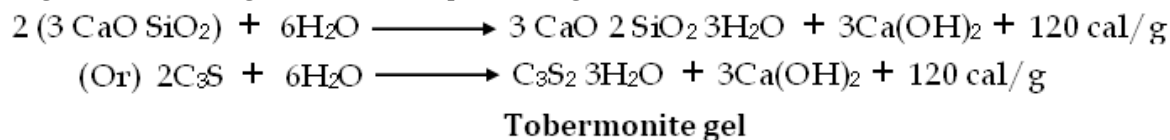


✓ Tetra calcium aluminoferrite undergoes hydration forming crystalline compound.

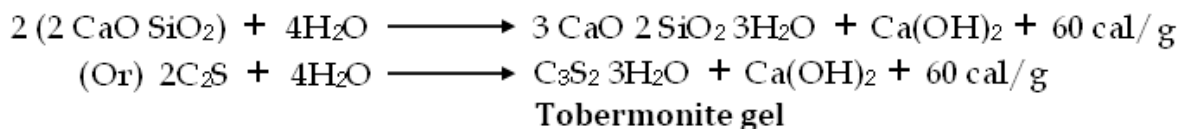


✓ Tri calcium silicate undergoes hydration slowly with in 7 days.

- Tobermonite gel acts as binding material and imparts strength to cement.

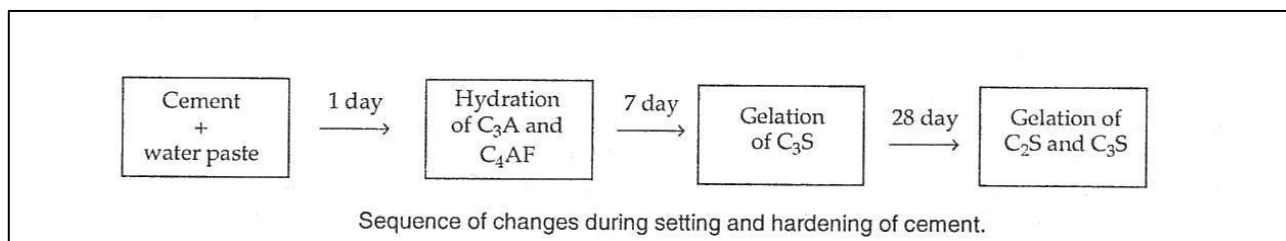


✓ The di calcium silicate reacts with water slowly in 7 – 28 days.



✓ These gels and crystalline products harden gradually to form hardened products.

- As hydration and hydrolysis proceeds, the strength and hardness of the set mass increase.
 - The process continues 10 – 28 days.
- Engineering properties of concrete is due to formation of Tobermonite gel.
- It has large surface area and strong adhesive strength.



25) Write a brief account on Decay of cement (or) deterioration of cement (or) How cement undergoes destruction.

➔ The cement concrete is easily attacked by salty water, CO₂, SO₂ and chlorides.

➔ Decay of cement is mainly due to

- Concrete cement contains free lime (CaO) which combines with CO₂ present in acidic water or air.
- The metal sulphates present in hard water combine with tri calcium aluminates to form expandable sulpho aluminates which are weak.
- Hydrolysis of aluminates also leads to decay of cement.

➔ Decay of cement is prevented by

- By coating the surface with epoxy resin paint or bituminous or linseed oil, which makes the surface impermeable to acidic water.
- By treating with silicon fluoride, CaF₂ is formed which prevents the penetration of acidic water into the capillaries.

Effect of carbon dioxide:

If concrete is exposed to an excessive CO₂ atmosphere during the first 24 hours of life, a soft, chalk like carbonate layer is formed.

- Carbonation occurs when CO₂ from air penetrates the concrete and reacts with calcium hydroxides to form carbonates.



- This reaction reduces the P^H of the pure solution to as low as 8.5, at which the passive film on the steel becomes weak.

Corrosion of concrete due to carbonation occurs in the areas of construction

- Where there is more rain fall
- The area shaded from sunlight
- The rein forced steel not covered by concrete

Carbonation of concrete lowers the amount of chloride ions needed for corrosion.

- In new concrete with a P^H 12 – 13, needs 7000 – 8000ppm chloride ions to start corrosion.
- If P^H is reduced to 10 – 11 due to carbonation, 100ppm chloride ions are enough to start corrosion.
- ◆ Carbonation destroys passive film on the reinforcement but not influence the rate of corrosion.

Effect of sulphur dioxide:

- ♣ SO₂ causes deterioration of cement concrete.
- ♣ This process of concrete deterioration by SO₂ is called sulphation.
- ♣ SO₂ corrodes more than CO₂.
- ♣ SO₂ is converted into H₂SO₃ followed by H₂SO₄ on combination with air and moisture.
- ♣ This H₂SO₄ combines with lime to form CaSO₄ which is weak.
- ♣ Water containing sulphates effects concrete.
- ♣ Tri calcium aluminate present in cement reacts with sulphate ions in the presence of lime to form calcium sulpho aluminate hydrates (Ettringite).
- ♣ The Ettringite expands and creates stress in the structure.
- ♣ This leads to cracking followed by disintegration.

Effect of chlorides:

- ♣ At P^H 12 – 13 in concrete, the steel is protected by self protective layer.
- ♣ This layer reduces the corrosion rate.
- ♣ Without the protective layer, steel would corrode more.
- ♣ The destruction of passive layer occurs when the P^H is reduced or chloride concentration increases to certain level.
- ♣ Chlorides dissolved in water can permeate through concrete cracks and cause corrosion.
- ♣ As the concentration of chloride ions increases, corrosion of steel increases.
- ♣ The rate of corrosion by chloride ions is influenced by
 - ☒ Availability of oxygen
 - ☒ Electrical resistivity
 - ☒ Relative humidity of the concrete
 - ☒ P^H and Temperature

